



Production of hydrogenated methyl esters of palm kernel and sunflower oils by employing rhodium and ruthenium catalytic complexes of hydrolysis stable monodentate sulfonated triphenylphosphite ligands

Christiana Vasiliou, Achilleas Bouriazos, Angeliki Tsihla, Georgios Papadogianakis*

National and Kapodistrian University of Athens, Department of Chemistry, Industrial Chemistry Laboratory, Panepistimiopolis-Zografou, 157 71 Athens, Greece

ARTICLE INFO

Article history:

Received 14 January 2014
Received in revised form 7 April 2014
Accepted 25 April 2014
Available online 5 May 2014

Keywords:

Hydrogenation
Methyl esters of palm kernel and sunflower oils
Rhodium
Sulfonated phosphites
Zero *trans*-fats

ABSTRACT

This study deals with the hydrogenation of renewable polyunsaturated methyl esters of palm kernel and sunflower oils to the saturated (C18:0) methyl stearate (MS) catalyzed by rhodium and ruthenium complexes modified with hydrolysis stable monodentate sulfonated triphenylphosphite (STPP) ligands under mild reaction conditions in the absence or presence of organic solvents. Superior selectivities up to 95.8 mol% of MS were achieved by Rh/STPP catalysts compared with the much lower selectivities (28.0–43.2 mol%) of MS obtained by rhodium catalysts modified with conventional triphenylphosphite or triphenylphosphine ligands. The bulkiness of transition metal STPP catalytic system which is in the form of a triisooctylammonium salt offers the possibility of the easy separation of the catalyst from the reaction mixture by means of a membrane. The hydrogenation reaction of the polyunsaturated C18 esters part of palm kernel oil and sunflower oil methyl esters toward the desired saturated product MS is an interesting catalytic reaction because it could act as a model reaction for studying the hydrogenation of edible vegetable oil triglycerides to hardfats. Hardfats can be further subjected to interesterification reactions with liquid edible vegetable oils to yield foodstuffs with zero amounts of *trans*-fats. Very recent investigations have questioned whether there really are direct associations between hardfat consumption and a higher cardiovascular disease risk. Furthermore, MS could be used as a starting material of selective heterogeneous catalytic hydrogenolysis reaction of the C18:0 fatty ester to the corresponding saturated C18:0 stearyl alcohol which is an important industrial fatty alcohol.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Vegetable oils and their derivatives are important feedstocks for the industry with a broad spectrum of applications such as in foodstuff chemistry, pharmacy, cosmetics, plastics, detergents, biolubricants and in the energy field with the production of 1st generation biodiesel fuel mainly by transesterification reactions with methanol to obtain fatty acid methyl esters (FAME's) [1–9]. Catalytic hydrogenation of renewable vegetable oils and their derivatives constitutes a major unit process in the chemical industry. In hydrogenation processes of C=C units in unsaturated fatty acids of vegetable oils heterogeneous catalytic systems based on nickel, palladium, copper, copper-chromite, platinum, etc. are

commonly used [1,2,5,7–9]. Heterogeneous nickel-based-catalyst was the choice of the edible oils hydrogenation industry which has a long history, started in 1902 with the first patent filed by Wilhelm Normann [10,11] for the liquid phase catalytic hydrogenation process of unsaturated fatty oils, in 1906 the British firm Joseph Crosfield & Sons developed the industrial hydrogenation process using as feedstock whale oil, and in 1911 the first commercial plant of Procter & Gamble went on stream with the appearance of the first industrially produced shortening, named “Crisco”, obtained by hydrogenation reactions using cottonseed oil feedstocks [12–15]. In the past, the so-called hardening processes of edible oil partial hydrogenation were carried out over commercial Ni-based heterogeneous catalysts in industrial scale which produced up to 45% *trans*-fats [15]. The aims of traditional hardening of edible oils were to increase their melting temperature and thus increasing the consistency for use as margarine and improving the oxidative stability while an important amount of the C=C units in the fatty acid chain

* Corresponding author. Tel.: +30 210 72 74 235; fax: +30 210 72 21 800.
E-mail address: papadogianakis@chem.uoa.gr (G. Papadogianakis).

was *cis/trans*-isomerized. In recent years the negative health effects of *trans*-fats received increasing attention because they were considered to be strongly correlated with a higher concentration of plasma LDL-cholesterol and consumption of *trans*-fats provides no apparent nutritional benefit and possesses a considerable potential for harm [16–23]. Regulations were introduced first in Denmark by January 2004 to restrict the use of industrially produced *trans*-fats in edible fats to 2 wt% in any food product making possible that people consume <1 g industrially produced *trans*-fats per day and decisions have been made in USA in January 2006 to declare the *trans*-isomers contained in fatty foodstuffs which resulted in a demand for products with lower *trans*-isomers content [16–23]. Therefore, there is increasing interest in the development of new industrial partial hydrogenation processes of edible oils producing low amounts or preferably zero amounts of *trans*-fats. There are several other methods to reduce *trans*-fats in foodstuffs such as blending, fractionation, interesterification and the most versatile way for producing zero *trans*-fats is the full hydrogenation of vegetable oils to saturated hardfats combined with interesterification reactions of liquid edible oils [19,20,22,24–38]. Interesterification reactions between fully hydrogenated fat and liquid vegetable oil involve changes in the distribution of the fatty acid moieties among the glycerides of the precursors compared to their original composition resulting in a change of the properties in the mixture [38]. Current cardiovascular guidelines encourage low consumption of saturated hardfats based on results of studies in the 1950s which showed that there is a direct association between consumption of saturated fats and cardiovascular disease (CVD). However, a very recent investigation [39] based on 76 studies with 659 300 participants (27 of these studies are randomized controlled trials possessing a higher strength of evidence with 103 000 participants) has not clearly provided supportive evidence for current cardiovascular guidelines that encourage low consumption of saturated hardfats. Further studies [40–42] have also questioned whether there really are associations between saturated hardfat consumption and higher CVD risks. Therefore, nutritional guidelines on saturated hardfats and cardiovascular guidelines as well, may require a reappraisal to reflect the results of current investigations.

It was demonstrated that one of us together with Fell and Bahrmann [43–46] developed a novel class of ligands namely monodentate and polydentate sulfonated phosphites which are hydrolysis stable systems and successfully applied in the rhodium catalyzed hydroformylation of olefins to produce aldehydes with higher selectivities toward the desired linear aldehydes, i.e. higher *n/iso*-aldehydes ratio of 80/20, with even higher rates compared to their corresponding rhodium catalysts modified with conventional triphenylphosphite (*n/iso* ratio=66/34) or triphenylphosphine (*n/iso* ratio=67/33) ligands under mild reaction conditions in organic solvents. Favre et al. [47] used such sulfonated phosphite ligands to modify rhodium catalysts for the hydroformylation of olefins in ionic liquids and could easily separate the organic phase containing the products from the ionic liquid phase containing the catalyst by a simple phase separation. Recycling experiments proved that the high *n/iso*-ratios of the aldehydes obtained with Rh/sulfonated phosphites, which were also higher compared to their corresponding rhodium catalysts modified with phosphines, remained high in two consecutive runs.

We report here the development of the hydrogenation of C=C units of renewable methyl esters of palm kernel and sunflower oils catalyzed by rhodium and ruthenium complexes modified with hydrolysis stable sulfonated triphenylphosphite (STPP) monodentate ligands in organic solvents [48]. The renewable FAME's of palm kernel and sunflower oils act as model raw materials for studying the full hydrogenation of their corresponding vegetable oils to hardfats which are to be further subjected to interesterification

reactions with liquid vegetable oils to yield foodstuffs with zero amounts of *trans*-fats. The bulkiness of the transition metal STPP catalytic system [48] which is in the form of a triisooctylammonium salt could offer the possibility of the easy separation of the catalyst from the reaction mixture by means of a membrane [63] which could be made from materials such as crosslinked polyolefins, poly(vinylidene fluoride), polyamides, etc. and this membrane catalyst separation technique has to be developed.

2. Experimental

2.1. Materials

Hydrogen (quality 5.0) was purchased from Air Liquide Hellas A.E.B.A. (Athens) and was used without further purification. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ were purchased from Acros Organics and Alfa Aesar, respectively, and both used as received. Methanol and toluene were purchased from SDS, diethyl ether from Sigma–Aldrich and methyl acetate from Merck–Schuchardt. All organic solvents before use were dried through activated molecular sieves 4 Å which were purchased from SDS and used after filtration over 0.2 µm filter unit (Millex-FG of Millipore). The 65 wt.% aqueous solution of 4-hydroxybenzenesulfonic acid, triisooctylamine and triphenylphosphite were purchased from Sigma–Aldrich. Triphenylphosphine was purchased from Fluka. Demineralized water was deoxygenated in an ultrasound bath under vacuum for 2 h. During the deoxygenation, the flask was disconnected from the vacuum, and the aqueous solvent was saturated with argon. To remove oxygen the procedure was repeated three times. The renewable starting materials methyl esters of palm kernel oil (Edenor® ME PK 12-18 F) and methyl esters of sunflower oil (Sunflower Fatty Acid ME®) were supplied by Cognis GmbH and used without any further purification.

2.2. Preparation of the sulfonated triphenylphosphite triisooctylammonium salt (STPP)

A 2000-ml five-necked, round-bottom flask, equipped with a mechanical stirrer, a thermometer, a dropping funnel and a condenser, which was previously evacuated, heated by a heat gun and filled at room temperature with argon, was charged with 160.5 g of a 65 wt.% aqueous solution of 4-hydroxybenzenesulfonic acid [104.3 g (0.6 mol) 4-hydroxybenzenesulfonic acid] and 150 ml of deoxygenated demineralized water. A mixture of 212.2 g (0.6 mol) triisooctylamine (TiOA) in 500 ml of dried toluene was added dropwise through the dropping funnel and stirred intensively for a period of 3 h at room temperature. After phase separation the colorless aqueous phase was discarded and the orange colored 4-hydroxybenzenesulfonic triisooctylammonium/toluene organic upper phase was dried over activated Na_2SO_4 for overnight. After separation of Na_2SO_4 by filtration, the 4-hydroxybenzenesulfonic triisooctylammonium/toluene organic phase, was heated under reflux in a Dean–Stark apparatus for 12 h to remove last amounts of water from the organic mixture.

A solution of 62.5 g (0.2 mol) triphenylphosphite and 5 g (0.01 mol) TiOA in 150 ml dried toluene was added dropwise to the 4-hydroxybenzenesulfonic triisooctylammonium/toluene mixture under stirring at 140 °C for 1 h. The condenser was then replaced by a distillation unit. Toluene was removed by distillation at 110 °C at first. The distillation of phenol, which is the byproduct of the transesterification reaction, was followed at 80–85 °C under 17 Torr vacuum within a period of 12 h and more phenol was distilled at 35 °C under 1 Torr for 6 h to give a total amount of 40.6 g of removed phenol. The yield of the transesterification reaction, based on the total amount of removed phenol by distillation,

was 72%. The unreacted triphenylphosphite was also removed by distillation at 65 °C under 0.01 Torr vacuum from the mixture and a yellow, highly viscous liquid remained which was the product mixture of the monodentate sulfonated triphenylphosphite triisooctylammonium salt (STPP) ligand. The purity of the STPP ligand is 95% regarding the content of sulfonated triphenylphosphite triisooctylammonium salts and was determined by quantitative $^{31}\text{P}\{^1\text{H}\}$ NMR analysis (121 MHz, referenced to external 85% H_3PO_4) on a Varian Unity Plus 300/54 spectrometer in CDCl_3 at 25 °C. δ : trisulfonated triphenylphosphite triisooctylammonium salt = +127.38 ppm; disulfonated triphenylphosphite triisooctylammonium salt = +127.95 ppm; monosulfonated triphenylphosphite triisooctylammonium salt = +128.35 ppm. ^1H NMR analysis of STPP (90 MHz; CDCl_3 ; 25 °C): δ = 7.85 ppm (d, $^4\text{NHR}_3$, 6H); 7.3–7.05 ppm (m, C_6H_4 , C_6H_5 , 39H); 3.01 ppm (m, NCH_2 , 6H); 1.83–0.7 ppm (m, CH_2 , CH_3 , 96H). Hydrolysis tests of STPP under very forcing conditions for a phosphite hydrolysis reaction (56 °C, molar ratio $\text{H}_2\text{O}/\text{STPP}$ = 30, STPP dissolved in acetone under intensive mechanical stirring) proved that STPP is much more stable against water compared with the conventional triphenylphosphite ligand. Under these conditions within 3 h of reaction time only 7.4% of STPP were hydrolysed compared with a quantitative (100%) hydrolysis of triphenylphosphite [43–46].

2.3. Typical hydrogenation procedure

The autoclave was thoroughly cleaned and followed by ten series of treatment of the autoclave at elevated temperature (110 °C) and pressure (50 bar of H_2) within 1 h each time in the presence of STPP/methanol and the absence of any transition metals in order to be sure that no memory effects of the autoclave regarding previous transition metal catalytic systems are still operative. The hydrogenation reactions of C=C units of methyl esters of palm kernel and sunflower oils were then performed in the presence of Rh- and Ru-STPP complexes in organic solvents and typical hydrogenation reaction conditions were given below. The Rh- or Ru-STPP catalyst precursor was first synthesized by dissolving the amount of STPP ligand in 20 ml of dried organic solvent and complexation with 1.32 mg (0.005 mmol) of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ or 1.31 mg (0.005 mmol) of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ under argon. The molar ratios of STPP/metal were from 3 to 5 because higher activities have been usually observed at low phosphite/metal molar ratios. The metal/STPP catalyst precursor solution was transferred into an *Autoclave Engineers* autoclave of a nominal volume of 100 ml which was previously evacuated and filled with argon together with the amount of methyl ester of palm kernel or sunflower oils. In the reaction mixture the molar ratios of C=C units/metal were from 300 to 500 and the transition metal concentrations were low from 24 to 28 ppm. After three pressurising-depressurising cycles with hydrogen to remove last traces of oxygen, the autoclave was pressured by H_2 and heated from 70 up to 110 °C with stirring (stirring rate = 850 rpm). At the reaction temperatures the hydrogen pressures were from 50 up to 100 bar. After 20 min up to 1 h the autoclave was cooled to room temperature and depressurized through a vent. The hydrogenation reaction mixture was removed and analyzed by gas chromatography (GC) after addition of tetradecane or eicosane as internal standards. Several hydrogenation reactions were repeated especially under the conditions where the obtained selectivities of the desired product methyl stearate were higher than 80 mol% in order to obtain reproducible results.

2.4. Analysis of the starting materials methyl esters of palm kernel and sunflower oils and the products of the hydrogenation reaction

During the hydrogenation reaction an amount of the starting material containing *cis*-olefinic bonds undergoes positional and

geometric isomerizations reactions to form several different positional and *trans*-isomers especially under the conditions where the selectivity to methyl stearate was below 50 mol%. These various *cis/trans*- and positional FAME isomers obtained as products in the mixture after the reaction and also the various FAME compounds in the starting materials of methyl esters of palm kernel and sunflower oils were identified by comparison of GC and GC/MS analytic data with data for authentic samples. GC/MS was measured on a Varian Star 3400CX GC coupled with a Varian Saturn 2000 ion trap MS and equipped with a flame ionization detector (FID) and a SP-2560 capillary column (100 m \times 0.25 mm i.d. \times 0.2 μm film thickness) which was purchased from Supelco (Athens, Greece). The SP-2560 capillary column is one of the two columns applied in the approved American Oil Chemists' Society (AOCS) official method Ce 1 h-05 for the determination of *cis*-, *trans*-, saturated, monounsaturated and polyunsaturated fatty acids in vegetable or non-ruminant animal oils and fats by capillary GLC method [49]. Carrier gas was He at 230 kPa. The oven temperature was initially set at 170 °C for 0 min and then increased to 220 °C with a rate of 1 °C/min. The injector and detector temperatures were set both at 220 °C. GC analyses were performed on a Shimadzu GC-14B equipped with a FID detector and with both columns a SP-2560 and an HP-Innowax capillary column. The GC conditions using the SP-2560 capillary column are the same as described above in GC/MS analyses. When using the HP-Innowax capillary column (30 m \times 0.251 mm i.d. \times 0.50 μm film thickness) which was purchased from Agilent Technologies the carrier gas was He at 150 kPa, the initial oven temperature was 170 °C followed by an increase to 240 °C with a rate of 3 °C/min. The injector and detector temperatures were 240 °C.

3. Results and discussion

3.1. Synthesis of the hydrolysis stable monodentate sulfonated triphenylphosphite triisooctylammonium salt (STPP)

The sulfonated triphenylphosphite triisooctylammonium salt (STPP) ligand (Fig. 1, $n=3$) was obtained by reaction of an aqueous 4-hydroxybenzenesulfonic acid solution with triisooctylamine (TiOA) in toluene and subsequent transesterification of the formed 4-hydroxybenzenesulfonic triisooctylammonium salt with triphenylphosphite to give (after removal of phenol by distillation) a mixture of sulfonated triphenylphosphite triisooctylammonium salts consisting of 56.34% of trisulfonated triphenylphosphite triisooctylammonium salt (TSTPP, $n=3$), 38.62% of disulfonated triphenylphosphite triisooctylammonium salt (DSTPP, $n=2$) and 5.04% of monosulfonated triphenylphosphite triisooctylammonium salt (MSTPP, $n=1$). The abbreviation STPP was used for this mixture of sulfonated triphenylphosphite triisooctylammonium salt ligands.

3.2. Catalytic hydrogenations of C=C units of methyl esters of vegetable oils

Recently, several papers have demonstrated that partial hydrogenation catalytic processes of polyunsaturated methyl esters of vegetable oils into their monounsaturated C18:1 counterparts (Scheme 1) without increasing the saturated C18:0 part are of great interest in the fields of production of high quality 1st generation biodiesel fuel and of biolubricants in terms of improved oxidative stability, energy and environmental performance at a low pour point. The catalytic systems applied in such hydrogenation reactions include water-soluble transition metal catalytic complexes in aqueous/organic two-phase systems [50–53], Rh/STPP complexes in organic solvents [54], conventional heterogeneous catalysts [55–62] and water-dispersible palladium(0) nanoparticles

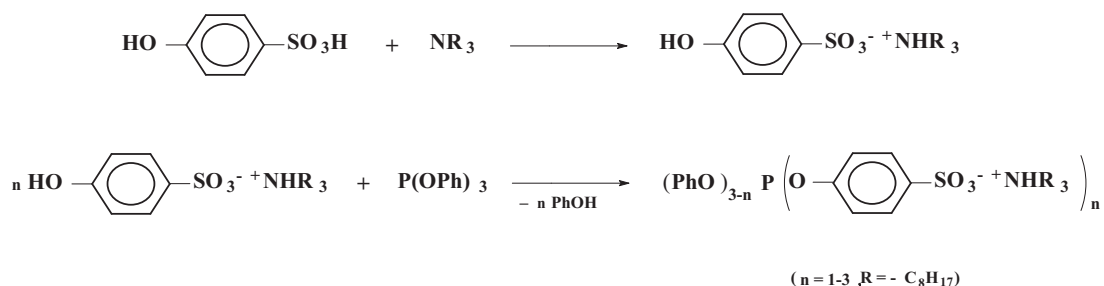
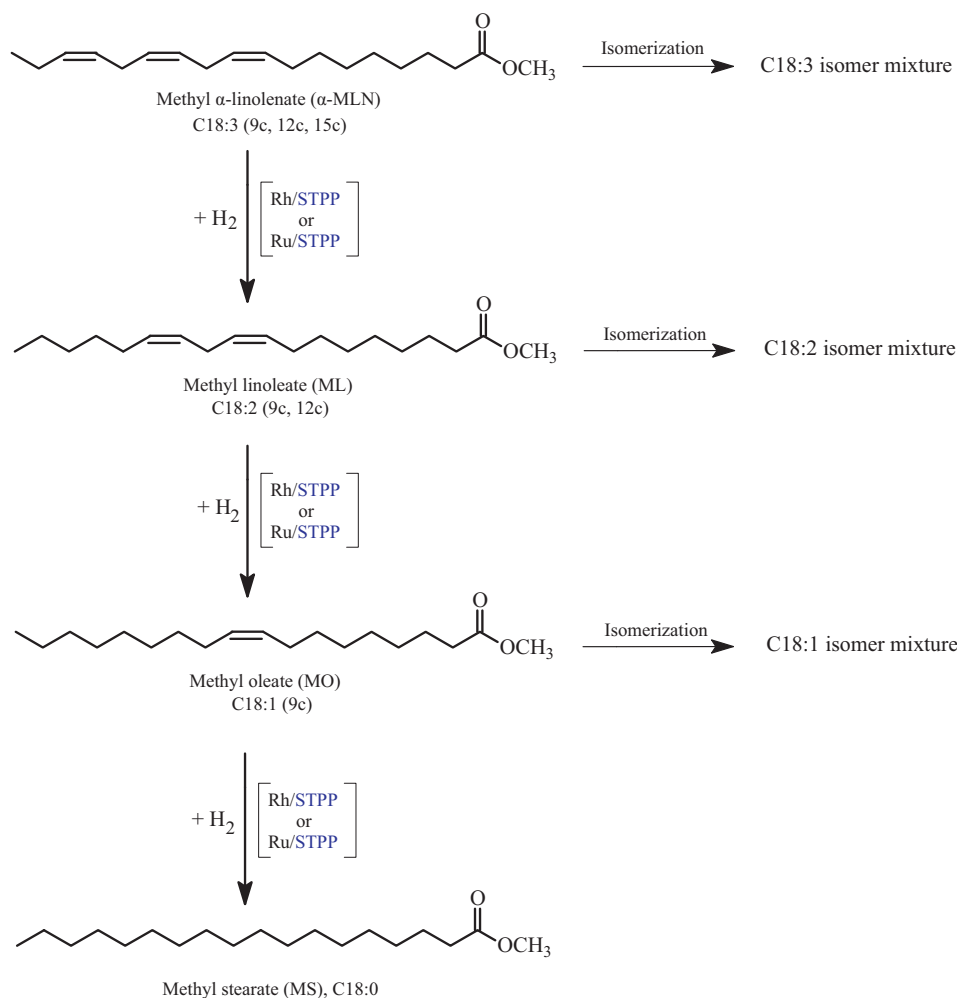


Fig. 1. Synthesis of sulfonated triphenylphosphite triisooctylammonium salts (STPP).

stabilized by water-soluble nitrogen-containing ligands in aqueous/organic two-phase systems [64]. Moreover, partial hydrogenation reactions possess a great potential to produce 2nd generation biodiesel from polyunsaturated fatty acid methyl esters (FAME) of alternative, non-food oil feedstocks which are originally not suitable for biodiesel production or give poor quality biodiesel fuel but combine the advantage that they would not affect food production [53,60]. In order to avoid deterioration in low-temperature behavior of biodiesel fuel such as on the pour point one of the aims of partial hydrogenation of polyunsaturated FAME's of vegetable oils is to obtain selectively the C18:1 esters without increasing the saturated methyl stearate C18:0 part. To preserve fluidity it

is mandatory not to increase the melting point of the mixture that depends on amount of methyl stearate (MS, C18:0) and both the extend of *cis/trans* and positional isomerization. For example the melting point of MS is +39.1 °C, of MO: −19.9 °C and of methyl elaidate (C18:1, 9t): +10.0 °C. To the best of our knowledge, this work is the first example of a catalytic hydrogenation of C=C units of renewable methyl esters of vegetable oils aimed to yield as desired product the saturated methyl stearate (C18:0 ester) and act as a model reaction for studying the full hydrogenation of vegetable oils to hardfats in order to be further subjected to interesterification reactions with liquid vegetable oils to yield foodstuffs with zero amounts of *trans*-fats.



Scheme 1. Hydrogenation of the unsaturated C18 esters part of methyl esters of palm kernel oil (MEPKO, Edenor® ME PK 12-18 F) and sunflower oil (MESO, Sunflower Fatty Acid ME®) to yield their saturated (C18:0) counterpart catalyzed by Rh- and Ru-STPP complexes in organic solvents. The term isomer mixture refers to all regio-isomers obtained from hydrogenation and/or positional isomerization (along the carbon chain) reactions and all other geometric isomers formed via *cis/trans* isomerization reactions.

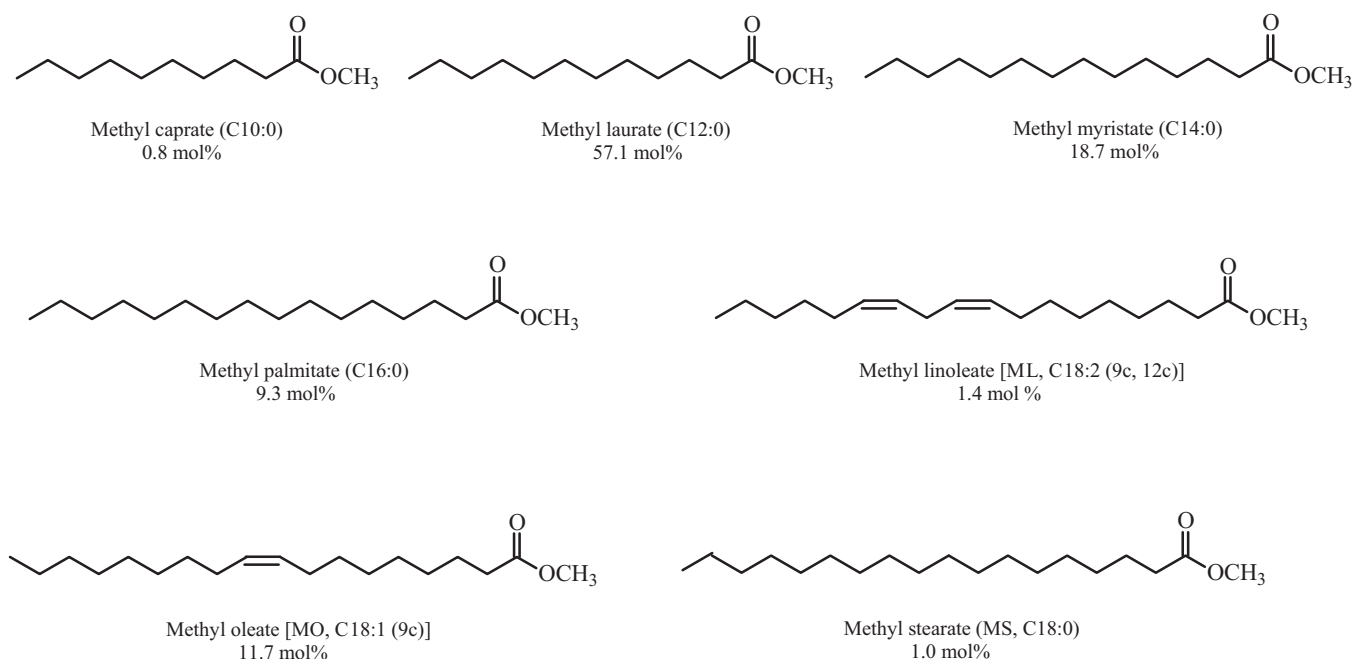


Fig. 2. Composition of the mixture of methyl esters of palm kernel oil (MEPKO, Edenor® ME PK 12–18 F, Cognis GmbH).

3.2.1. Hydrogenation of C=C units of methyl esters of palm kernel oil (MEPKO) catalyzed by Ru- and Rh-STPP complexes

The mixture of methyl esters of palm kernel oil (Fig. 2) of Cognis GmbH (Edenor® ME PK 12–18 F) was used as starting material in the hydrogenation reactions of the unsaturated C18 esters part contained only 14.1 mol% of C18 FAME's with the proportion of 1.0 mol% methyl stearate (MS, C18:0), 11.7 mol% methyl oleate [MO, C18:1 (9c)] and 1.4 mol% methyl linoleate [ML, C18:2 (9c,12c)]. The content of C18 FAME's was then calculated to 100 mol% to give 7.1 mol% of C18:0 ester, 83.0 mol% of C18:1 compound and 9.9 mol% of the C18:2 ester (Table 1). Except the C18 FAME compounds the mixture of methyl esters of palm kernel oil (MEPKO) further contained the following saturated esters (Fig. 2): 0.8 mol% methyl caprate (C10:0), 57.1 mol% methyl laurate (C12:0), 18.7 mol% methyl myristate (C14:0) and 9.3 mol% methyl palmitate (C16:0) which do not contain C=C double bonds and were ignored in the calculations to adjust the C=C units/metal molar ratios in the catalytic reactions and the presence of a major amount of saturated C10:0–C16:0 fatty esters in the reaction mixture has probably a minor effect on the activity and selectivity of the hydrogenation reaction of C=C units of C18 fatty esters catalyzed by transition metal complexes modified with STPP ligands in polar organic solvents such as methanol.

Table 1 shows the selectivity of rhodium catalytic complexes modified with STPP ligands as a function of temperature and hydrogen pressure and of Ru/STPP complexes at 100 °C, 80 and 100 bar and C=C units/Ru molar ratios of 500 and 300 in the hydrogenation of the unsaturated C18 esters part of MEPKO to yield the desired saturated product methyl stearate (Scheme 1, MS, C18:0) in methanol. Initially, we investigated the influence of hydrogen pressure on the reduction of the C=C double bonds of MEPKO catalyzed by ruthenium complexes modified with STPP ligands. The catalytic selectivity toward the C18:0 ester slightly decreases with increasing hydrogen pressure from 80 up to 100 bar to give selectivities to C18:0 from 36.3 mol% to 35.4 mol% (Table 1, entries 1/1 and 1/2). This small difference with a minor decrease in the selectivity of MS was within of measurement error range to obtain reproducible results. At a lower molar ratio of C=C units/Ru = 300, a reaction temperature of 100 °C and 80 bar of hydrogen pressure

the selectivity to the saturated product increases to give 45.8 mol% of the C18:0 ester (Table 1, entry 1/3) compared with 36.3 mol% of MS obtained at the higher C=C units/Ru molar ratio of 500 (Table 1, entry 1/1). A comparative hydrogenation experiment of MEPKO catalyzed by rhodium complexes modified with STPP ligands was performed at a molar ratio of C=C units/Rh = 300 and TSTPP/Rh = 4, at 100 °C and 80 bar of hydrogen pressure for 60 min in methanol which revealed that the selectivity of Rh/STPP catalysts to methyl stearate was much higher namely 76.0 mol% of C18:0 ester (Table 1, entry 1/4) compared with the selectivity obtained by the use of Ru/STPP catalysts which was only 45.8 mol% of MS (Table 1, entry 1/3). The selectivities in the hydrogenation of the polyunsaturated C18 esters part of MEPKO toward the desired saturated product methyl stearate increase with increasing temperature from 70 °C up to 80 °C to give selectivities from 86.0 mol% up to 95.8 mol% of the saturated C18:0 ester product at a molar ratio of C=C units/Rh = 300 and STPP/Rh = 4 and a hydrogen pressure of 80 bar at a rhodium concentration of 28 ppm in methanol (Table 1, entries 1/7, 1/8 and Fig. 3). Raising the reaction temperature over 80 °C a negative effect on the selectivity to methyl stearate could be observed in the hydrogenation of the unsaturated part of MEPKO to give from 90 °C up to 110 °C selectivities from 81.7 mol% down to 63.6 mol% of the C18:0 ester (Table 1, entries 1/4–1/6, Fig. 3). The effect of yield increase at the temperatures from 70 to 80 °C and decrease at the temperatures from 80 °C and above could probably be explained by a catalytically active key species which at 80 °C effectively lowered the activation energy barrier at the rate determining step of the MEPKO hydrogenation reaction which is not favored at lower temperatures whereas at higher temperatures the catalytic active key species is destabilized. Similarly, the best results regarding the lower formation of undesired *trans*-C18:1 esters of only 3.7 mol% (Fig. 3, Table 1, entry 1/7) were obtained at the temperature of 80 °C probably because at this temperature the Rh/STPP catalytically active key species exhibited the highest catalytic activity in the hydrogenation of the *trans*-C18:1 isomers to yield MS. In general, the *trans*-isomers were more difficult hydrogenated compared with their *cis*-counterparts. At higher temperatures the catalytic hydrogenation activity was decreased in addition to the effect that higher temperatures favored the *cis/trans*-isomerisation

Table 1

Hydrogenation of the polyunsaturated C18 esters part of methyl esters of palm kernel oil (MEPKO, Edenor® ME PK 12-18 F)^a to their saturated (C18:0) counterpart catalyzed by Ru- and Rh-STPP complexes in methanol.^b

Entry	Catalyst precursor	C=C/M molar ratio	T (°C)	P _{H₂} (bar)	C18:2 total (mol%)	C18:1 total (mol%)	cis-C18:1 total (mol%)	trans-C18:1 total (mol%)	C18:0 (mol%)	TON ^c
MEPKO ^a	–	–	–	–	9.9 ^d	83.0 ^e	83.0 ^e	–	7.1	–
1/1	RuCl ₃ ·3H ₂ O/STPP	500	100	80	2.3	61.4	40.4	21.0	36.3	146
1/2	RuCl ₃ ·3H ₂ O/STPP	500	100	100	2.5	62.1	42.7	19.4	35.4	141
1/3	RuCl ₃ ·3H ₂ O/STPP	300	100	80	2.0	52.2	39.7	12.5	45.8	116
1/4	RhCl ₃ ·3H ₂ O/STPP	300	100	80	0.0	24.0	1.8	22.2	76.0	207
1/5	RhCl ₃ ·3H ₂ O/STPP	300	110	80	0.5	35.9	4.7	31.2	63.6	169
1/6	RhCl ₃ ·3H ₂ O/STPP	300	90	80	0.4	17.9	1.3	16.6	81.7	224
1/7	RhCl ₃ ·3H ₂ O/STPP	300	80	80	0.5	3.7	0.0	3.7	95.8	266
1/8	RhCl ₃ ·3H ₂ O/STPP	300	70	80	0.5	13.5	0.1	13.4	86.0	237
1/9	RhCl ₃ ·3H ₂ O/STPP	300	80	50	0.5	15.4	0.2	15.2	84.1	231

^a The starting material methyl esters of palm kernel oil (MEPKO, Edenor® ME PK 12-18 F) which is a product of Cognis GmbH except the C18 compounds (14.1 mol%) further contains: 0.8 mol% methyl decanoate (C10:0), 57.1 mol% methyl dodecanoate (C12:0), 18.7 mol% methyl tetradecanoate (C14:0) and 9.3 mol% methyl palmitate (MP, C16:0). The C18 esters total content of 14.1 mol% with the proportion of 1.0 mol% methyl stearate (C18:0), 11.7 mol% methyl oleate (C18:1) and 1.4 mol% methyl linoleate (C18:2) was calculated to 100 mol% to give 7.1 mol% of C18:0 ester, 83.0 mol% of C18:1 compound and 9.9 mol% of C18:2 ester.

^b Reaction conditions: *t* = 60 min; 1.32 mg (0.005 mmol) RhCl₃·3H₂O; 1.31 mg (0.005 mmol) RuCl₃·3H₂O; 28.01 mg (0.02 mmol) TSTPP (P/M molar ratio = 4); 3.208 g (1.5 mmol of C=C units of the unsaturated C18 esters part) of Edenor® ME PK 12-18 (C=C units/M molar ratio = 300) in entries 1/3–1/9; 20 ml methanol; [Rh] = 28 ppm; [Ru] = 24 ppm, except in entry 1/3 [Ru] = 26 ppm. Stirring rate = 850 rpm.

^c Turnover number (TON). Defined as mole of hydrogenated C=C units in the C18:2 and C18:1 compounds in the starting material mixture and all other regiomers formed during the course of the reaction per mole of transition metal.

^d Methyl linoleate (ML), C18:2 (9c, 12c).

^e Methyl oleate (MO), C18:1 (9c).

reaction and at 110 °C the selectivity to *trans*-C18:1 esters was enormously increased to 31.2 mol% (Fig. 3, Table 1, entry 1/5). The effect of hydrogen pressure on the Rh/STPP catalyzed hydrogenation of unsaturated MEPKO is shown in Table 1, entries 1/7 and 1/9. At 80 °C the catalytic selectivity of Rh/STPP complexes toward the desired product C18:0 ester increases with increasing hydrogen pressure from 50 to 80 bar to give selectivities to C18:0 ester from 84.1 mol% to 95.8 mol% (Table 1, entries 1/9 and 1/7).

It is relevant to point out that the saturated C10:0–C18:0 esters obtained in the Ru- and Rh/STPP-catalyzed hydrogenation of MEPKO (Fig. 2) could be used as feedstocks for heterogeneously catalyzed hydrogenolysis reactions of saturated fatty esters to their corresponding saturated fatty alcohols. Industrially applied heterogeneous Adkins-type ZnO/Cr₂O₃/Al₂O₃ or CdO/Cr₂O₃/Al₂O₃ hydrogenolysis catalysts are active only for hydrogenolysis reactions of fatty ester moieties to fatty alcohols and are not able

to hydrogenate C=C units even under forcing conditions such as 200–350 °C and 250–300 bar hydrogen pressure typical conditions of industrial processes for the manufacture of fatty alcohols [1,2]. Renewable MEPKO mixtures are excellent starting materials for industrial catalytic hydrogenolysis processes to produce their corresponding fatty alcohols which are further used for manufacturing of surfactants, emulsifiers, lubricants and plasticizers [1,2].

3.2.2. Hydrogenation of methyl esters of sunflower oil (MESO) catalyzed by Rh- and Ru-STPP complexes

Table 2 presents the activity and selectivity of catalytic complexes of rhodium modified with STPP, PPh₃ and P(OPh)₃ ligands as well as of Ru/STPP catalysts as a function of temperature, hydrogen pressure, STPP/Metal molar ratio, presence and absence of different organic solvents and of reaction time in the hydrogenation of polyunsaturated methyl esters of sunflower oil (MESO). To obtain

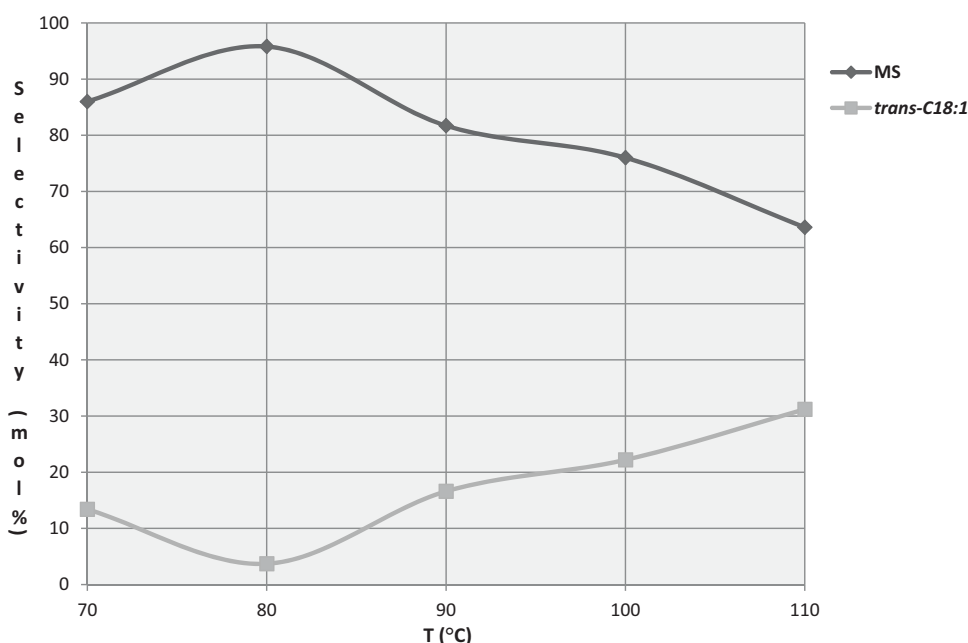


Fig. 3. Plot of the selectivities of MS and *trans*-C18:1 esters versus temperature in the Rh/STPP catalyzed hydrogenation of MEPKO.

Table 2

Hydrogenation of methyl esters of sunflower oil (MESO, Sunflower Fatty Acid ME[®])^a catalyzed by rhodium complexes modified with STPP, PPh₃ and P(OPh)₃ ligands as well as Ru/STPP complexes in various organic solvents.^b

Entry	Catalyst precursor	L/M molar ratio	T (°C)	P _{H₂} (bar)	t (min)	Solvent	C18:3 total (mol%)	C18:2 total (mol%)	C18:1 total (mol%)	cis-C18:1 total (mol%)	trans-C18:1 total (mol%)	C18:0 (mol%)	TON ^c
MESO ^a	–	–	–	–	–	–	1.2 ^d	63.3 ^e	32.0 ^f	32.0 ^f	–	3.5	–
2/1	RhCl ₃ ·3H ₂ O/STPP	3	110	50	60	MeOH	0.6	0.0	22.0	2.0	20.0	77.4	370
2/2	RhCl ₃ ·3H ₂ O/STPP	4	110	50	60	MeOH	0.6	0.0	19.4	1.8	17.6	80.0	382
2/3	RhCl ₃ ·3H ₂ O/STPP	5	110	50	60	MeOH	0.0	10.6	65.6	26.8	38.8	23.8	270
2/4	RhCl ₃ ·3H ₂ O/STPP	4	110	30	60	MeOH	0.1	4.8	57.7	12.9	44.8	37.4	298
2/5	RhCl ₃ ·3H ₂ O/STPP	4	100	50	60	MeOH	1.0	0.0	12.0	0.5	11.5	87.0	418
2/6	RhCl ₃ ·3H ₂ O/STPP	4	90	50	60	MeOH	1.1	13.2	58.6	24.4	34.2	27.1	251
2/7	RhCl ₃ ·3H ₂ O/STPP	4	100	50	60	–	1.5	58.8	33.3	31.8	1.5	6.4	21
2/8	RhCl ₃ ·3H ₂ O/STPP	4	100	50	60	Ether	0.0	62.3	33.0	33.0	0.0	4.7	11
2/9	RhCl ₃ ·3H ₂ O/STPP	4	100	50	60	MeOAc	1.6	59.6	33.3	32.6	0.7	5.5	16
2/10	RhCl ₃ ·3H ₂ O/PPh ₃	4	100	50	60	MeOH	1.0	4.4	51.4	16.3	35.1	43.2	296
2/11	RhCl ₃ ·3H ₂ O/P(OPh) ₃	4	100	50	60	MeOH	2.4	8.8	60.8	31.5	29.3	28.0	267
2/12	RuCl ₃ ·3H ₂ O/STPP	4	100	50	60	MeOH	0.0	3.0	44.4	22.8	21.6	52.6	308
2/13	RuCl ₃ ·3H ₂ O/STPP	4	100	80	60	MeOH	0.0	0.6	10.2	0.0	10.2	89.2	429
2/14	RuCl ₃ ·3H ₂ O/STPP	4	100	80	20	MeOH	2.4	20.9	49.0	41.4	7.6	27.7	206
2/15	RhCl ₃ ·3H ₂ O/STPP	4	100	50	20	MeOH	1.2	16.3	60.3	31.9	28.7	21.9	233

^a The starting material of methyl esters of sunflower oil (Sunflower Fatty Acid ME[®]) which is a product of Cognis GmbH except the C18 compounds with a total content of 94.1 mol% further contains 5.3 mol% methyl palmitate (MP, C16:0) and 0.6 mol% of methyl docosanoate (MD, C22:0) which were ignored in the experiments. The C18 esters total content of 94.1 mol% with the proportion of 1.1 mol% methyl linolenate (C18:3), 59.6 mol% methyl linoleate (C18:2), 30.1 mol% methyl oleate (C18:1) and 3.3 mol% methyl stearate (C18:0) was calculated to 100 mol% to give 1.2 mol% of C18:3 ester, 63.3 mol% C18:2 ester, 32.0 mol% C18:1 ester and 3.5 mol% C18:0 ester.

^b Reaction conditions: 1.32 mg (0.005 mmol) RhCl₃·3H₂O; 1.31 mg (0.005 mmol) RuCl₃·3H₂O; 0.539 g (2.5 mmol of C=C units) of methyl esters of sunflower oil (C=C units/metal molar ratio = 500); 20 ml of organic solvent. Stirring rate = 850 rpm.

^c Turnover number (TON). Defined as mole of hydrogenated C=C units in the C18:3, C18:2 and C18:1 compounds in the starting material mixture and all other regiomers formed during the course of the reaction per mole of transition metal.

^d Methyl α-linolenate (α-MLN), C18:3 (9c, 12c, 15c).

^e Methyl linoleate (ML), C18:2 (9c, 12c).

^f Methyl oleate (MO), C18:1 (9c).

their saturated counterpart methyl stearate (Scheme 1, MS, C18:0) a C=C units/metal molar ratio of 500 was used in the homogeneous catalytic reaction medium. The hydrogenation reaction of MESO to MS is an interesting catalytic reaction because it could act as a model reaction for studying the full hydrogenation of edible oils to saturated hardfats which could be further used as feedstocks with liquid edible oils in interesterification reactions to yield foodstuffs with zero amounts of *trans*-fats. Furthermore, MS obtained as product from the Rh- and Ru-STPP catalyzed hydrogenation of MESO could be further applied as feedstock for industrial heterogeneously catalyzed hydrogenolysis reactions to obtain stearyl alcohol which is regarded as an important fatty alcohol. The rhodium catalyzed hydrogenation reaction of MESO to the saturated C18:0 ester is strongly influenced by the amount of STPP ligand added to the rhodium precursor. The effect of STPP/Rh molar ratio is shown in Table 2, entries 2/1–2/3. The highest selectivity of 80.0 mol% of the desired C18:0 ester was obtained when TSTPP/Rh = 4 (entry 2/2). Lower selectivity of 77.4 mol% of saturated MS was observed at the lower STPP/Rh molar ratio of 3 (entry 2/1) and the selectivity to the desired product dramatically decreased to give 23.8 mol% of the C18:0 ester at the higher STPP/Rh molar ratio of 5 (entry 2/3). This lower formation of the end product of the catalytic hydrogenation reaction namely the saturated C18:0 ester and therefore of the lower catalytic activity observed at higher STPP/Rh molar ratios could probably be explained by a competition between the free STPP ligand and the C=C units of FAME starting material for a coordination site on rhodium takes place which may lead to a retardation in the activation of the MESO hydrogenation reaction to yield the saturated MS ester. The effect of hydrogen pressure on the Rh/STPP catalyzed hydrogenation of MESO is shown in entries 2/2 and 2/4. High selectivities to C18:0 ester (80.0 mol%) were obtained at a pressure of 50 bar of dihydrogen (entry 2/2) and the selectivity to MS decreased at a lower hydrogen pressure of 30 bar to give 37.4 mol% of C18:0 ester (entry 2/4). The effect of temperature is presented in entries 2/2, 2/5 and 2/6. The highest selectivity to saturated C18:0 ester of 87.0 mol% was achieved at a reaction temperature of 100 °C (entry 2/5) and the selectivity to MS decreased to

80.0 mol% with increasing the reaction temperature to 110 °C (entry 2/2). Using a lower temperature of 90 °C the catalytic selectivity drops dramatically in the hydrogenation reaction and the saturated C18:0 ester was formed only to 27.1 mol% (entry 2/6). A comparison regarding the maximum yields achieved in the hydrogenation of MEPKO and MESO as a function of temperature showed that with MEPKO it was achieved at 80 °C (Table 1, entry 1/7) whereas with MESO at 100 °C (Table 2, entry 2/5). This could probably be explained due to the higher polarity of the hydrogenation reaction medium of MERKO because it contains mainly (85.9 mol%) more polar C10:0–C16:0 FAMES and only 14.1 mol% of C18 FAMES whereas MESO contained 94.1 mol% of C18 FAMES. The rhodium catalyzed hydrogenation reaction of MESO to the saturated C18:0 ester is strongly influenced by the nature of the added organic solvent (Table 2, entries 2/5, 2/8, 2/9). Very low catalytic activities and selectivities toward the C18:0 ester were observed when diethyl ether was used as a solvent and MS was formed only to 4.7 mol% (entry 2/8). The selectivity toward C18:0 ester could be slightly increased to 5.5 mol% with more polar methyl acetate (entry 2/9). An enormous increase in catalytic activity and selectivity to MS was achieved using methanol which is a more polar and protic organic solvent and the C18:0 ester was formed with 87.0 mol% (entry 2/5). This enormous higher catalytic activity in the presence of methanol compared with other organic solvents could probably be rationalized by assuming that methanol fine tunes the coordination sphere of rhodium by coordination of methanol molecules on the sites of rhodium and the σ-donation of coordinated methanol probably increases the electron density on the catalytically active rhodium sites which probably are electron-poor metal centers due to coordination of highly π-acidic STPP ligands. In the absence of any added organic solvent (entry 2/7) very low catalytic activities and selectivities to MS (6.4 mol%) were observed probably of poor mixing and of lower polarity of MESO which acted in this case both as starting material and as solvent. The hydrogenation reaction of MESO was performed using rhodium compounds modified with conventional modifiers such as triphenylphosphite [P(OPh)₃] as a more basic ligand and triphenylphosphine (PPh₃) as a much more basic ligand

than STPP. The results are summarized in entries 2/5, 2/10 and 2/11. Lower selectivities to MS (43.2 mol%) were obtained in the hydrogenation of MESO using Rh/PPh₃ catalysts (entry 2/10) and a much lower formation of C18:0 ester (28.0 mol%) was observed with the Rh/P(OPh)₃ catalytic complexes (entry 2/11) compared with the selectivity to MS of 87.0 mol% achieved by Rh/STPP catalysts (entry 2/5). A similar effect was also observed in hydroformylation reactions of olefins where with the Rh/STPP catalysts higher selectivities toward the desired linear aldehydes and even higher rates were obtained compared with the activities and selectivities exhibited by conventional Rh/PPh₃ or Rh/P(OPh)₃ catalytic complexes [43–46]. The subsequent hydrogenation reactions were carried out with ruthenium catalytic complexes and in order to be sure that no memory effects of the autoclave regarding the transition metal rhodium are still operative the autoclave was thoroughly cleaned and followed by several series of treatment of the reactor at elevated temperatures (110 °C) and pressures (50 bar of H₂) within 1 h each time in the presence of STPP/methanol and in the absence of any transition metal. A high selectivity to MS of 89.2 mol% with a high catalyst productivity of 429 turnover number (TON) and a selectivity to *trans*-C18:1 esters of 10.2 mol% were obtained at a hydrogen pressure of 80 bar (entry 2/13) in the Ru/STPP catalyzed hydrogenation of MESO compared to the selectivities of 52.6 mol% of MS and of 21.6 mol% of *trans*-C18:1 esters observed at a lower pressure of 50 bar of dihydrogen (entry 2/12) within 60 min of reaction time in methanol as a solvent. At a shorter reaction time of 20 min at a hydrogen pressure of 80 bar in the Ru/STPP catalyzed hydrogenation reaction the selectivity to C18:0 ester drops dramatically to give only 27.7 mol% of MS and a lower selectivity to *trans*-C18:1 esters of 7.6 mol% (entry 2/14). In the Rh/STPP catalyzed hydrogenation reaction of MESO at a shorter reaction time of 20 min and a pressure of 50 bar of dihydrogen a lower selectivity of 21.9 mol% of MS and a higher selectivity to *trans*-C18:1 esters of 28.7 mol% (entry 2/15) were observed compared with the selectivity of 87.0 mol% of MS and of 11.5 mol% of *trans*-C18:1 esters obtained at a longer reaction time of 60 min (entry 2/5).

4. Conclusions

We have shown that the hydrogenation reaction of renewable polyunsaturated methyl esters of palm kernel and sunflower oils to the saturated product methyl stearate (MS) using transition metal catalytic complexes modified with hydrolysis stable monodentate sulfonated triphenylphosphite ligands proceeds smoothly in the absence or presence of organic solvents such as methanol. Much higher selectivities up to 95.8 mol% of the saturated C18:0 ester were achieved with transition metal catalytic complexes modified with sulfonated triphenylphosphite ligands compared with the selectivities obtained with their corresponding complexes modified by conventional triphenylphosphite or triphenylphosphine ligands. The bulkiness of the transition metal sulfonated triphenylphosphite catalytic system which is in the form of a triisooctylammonium salt could offer the possibility of the easy separation of the catalyst from the reaction mixture by means of a membrane made from materials such as crosslinked polyolefins, poly(vinylidene fluoride), polyamides, etc. and this membrane catalyst separation technique has still to be developed. The hydrogenation reaction of the polyunsaturated C18 esters part of palm kernel oil and sunflower oil methyl esters toward the desired saturated product MS is an interesting catalytic reaction because it could act as a model reaction for studying the full hydrogenation of edible vegetable oil triglycerides to hardfats to be further subjected to interesterification reactions with liquid edible vegetable oils to yield foodstuffs with zero amounts of *trans*-fats and furthermore because the saturated product MS could be used as a starting

material for the selective heterogeneous catalytic hydrogenolysis reaction of the C18:0 fatty ester to the corresponding saturated C18:0 stearyl alcohol which is an important industrial fatty alcohol. Hence, we are currently investigating the scope of this useful hydrogenation reaction of renewable unsaturated methyl esters of vegetable oils to yield methyl stearate employing transition metal catalytic complexes modified with sulfonated phosphites.

Acknowledgments

Financial support of this research by the Postgraduate Studies Programme on “Catalysis an Integrated Approach” of Epeaek II Programme of Greek Ministry of Education and the European Union (75/25) and by the Special Account for Research Grants of the Research Committee of the National and Kapodistrian University of Athens under contract 70/4/7568 are gratefully acknowledged. We thank Cognis GmbH for the supply of the starting materials methyl esters of palm kernel oil (Edenor[®] ME PK 12–18 F) and of methyl esters of sunflower oil (Sunflower Fatty Acid ME[®]).

References

- [1] A. Corma, S. Iborra, A. Vely, *Chem. Rev.* 107 (2007) 2411–2502.
- [2] T. Turek, D.L. Trimm, N.W. Cant, *Catal. Rev. Sci. Eng.* 36 (1994) 645–683.
- [3] T. Issariyakul, A.K. Dalai, *Renew. Sustain Energy Rev.* 31 (2014) 446–471.
- [4] B.R. Moser, *Biofuels* 5 (2014) 5–8.
- [5] W. Rupilius, S. Ahmad, *Eur. J. Lipid Sci. Technol.* 109 (2007) 433–439.
- [6] G.W. Huber, S. Iborra, A. Corma, *Chem. Rev.* 106 (2006) 4044–4098.
- [7] A. Behr, N. Döring, S. Durowicz-Heil, B. Ellenberg, Ch. Kozik, Ch. Lohr, H. Schmidke, *Fat Sci. Technol.* 95 (1993) 2–12.
- [8] T. Schaff, H. Greven, *Lipid Technol.* 22 (2010) 31–35.
- [9] V.A. Pozdeev, S.P. Safronov, S.V. Levanova, E.L. Krasnykh, *Russ. J. Appl. Chem.* 85 (2012) 261–266.
- [10] W. Normann, *DRP* 141 029 (1902).
- [11] G. Leuteritz, *Fette Seifen Anstrichmittel* 71 (1969) 441–445.
- [12] G.R. List, M.A. Jackson, *Inform* 18 (2007) 403–405.
- [13] G.R. List, M.A. Jackson, *Inform* 20 (2009) 395–397.
- [14] A. Philippaerts, P.A. Jacobs, B.F. Sels, *Angew. Chem. Int. Ed.* 52 (2013) 5220–5226.
- [15] G.R. List, *Inform* 23 (2012) 451–453.
- [16] A. Bysted, A.E. Mikkelsen, T. Leth, *Eur. J. Lipid Sci. Technol.* 111 (2009) 574–583.
- [17] Ch.D. Hillyer, *Inform* 18 (2007) 356–357.
- [18] P.M. Clifton, J.B. Keogh, M. Noakes, *J. Nutr.* 134 (2004) 874–879.
- [19] M.R. L'Abbé, S. Stender, M. Skeaff, Ghafoorunissa M. Tavella, *Eur. J. Clin. Nutr.* 63 (2009) 550–567.
- [20] J.E. Hunter, *Nutr. Res.* 25 (2005) 499–513.
- [21] R.H. Eckel, S. Borra, A.H. Lichtenstein, S.Y. Yin-Piazza, *Circulation* 115 (2007) 2231–2246.
- [22] D. Mozaffarian, M.B. Katan, A. Ascherio, M.J. Stampfer, W.C. Willett, *N. Engl. J. Med.* 354 (2006) 1601–1613.
- [23] D. Schleifer, *Soc. Stud. Sci.* 43 (2012) 54–77.
- [24] M.T. Tarrago-Trani, K.M. Phillips, L.E. Lemar, J.M. Holden, *J. Am. Diet. Assoc.* 106 (2006) 867–880.
- [25] A.P.B. Ribeiro, R. Grimaldi, L.A. Gioielli, L.A.G. Gonçalves, *Food Res. Int.* 42 (2009) 401–410.
- [26] P. Adhikari, J.-A. Shin, J.-H. Lee, H.-R. Kim, I.-H. Kim, S.-T. Hong, K.-T. Lee, *Food Bioprocess Technol.* 5 (2012) 2474–2487.
- [27] L. Zhang, H. Muramoto, S. Ueno, K. Sato, *J. Oleo Sci.* 60 (2011) 287–292.
- [28] D. Li, P. Adhikari, J.-A. Shin, J.-H. Lee, Y.-J. Kim, X.-M. Zhu, J.-N. Hu, J. Jin, C.C. Akoh, K.-T. Lee, *LWT Food Sci. Technol.* 43 (2010) 458–464.
- [29] A.P.B. Ribeiro, R.C. Basso, R. Grimaldi, L.A. Gioielli, A.O. dos Santos, L.P. Gardoso, L.A.G. Gonçalves, *Food Res. Int.* 42 (2009) 1153–1162.
- [30] A.P.B. Ribeiro, R.C. Basso, R. Grimaldi, L.A. Gioielli, L.A.G. Gonçalves, *J. Food Lipids* 16 (2009) 362–381.
- [31] I.-H. Kim, S.-M. Lee, B.-M. Lee, H.-K. Park, J.-Y. Kim, K.-I. Kwon, J.-W. Kim, J.-S. Lee, Y.-H. Kim, *J. Agric. Food Chem.* 56 (2008) 5942–5946.
- [32] M. Criado, E. Hernández-Martín, A. López-Hernández, C. Otero, *J. Am. Oil Chem. Soc.* 84 (2007) 717–726.
- [33] J. Farmani, M. Hamed, M. Safari, A. Madadlou, *Food Chem.* 102 (2007) 827–833.
- [34] V. Petrauskaitė, W. de Greyt, M. Kellens, A. Huyghebaert, *J. Am. Oil Chem. Soc.* 75 (1998) 489–493.
- [35] S. Schmidt, S. Hurtová, J. Zemanovič, S. Sekretár, P. Šimon, P. Ainsworth, *Food Chem.* 55 (1996) 343–348.
- [36] S. Hurtová, S. Schmidt, J. Zemanovič, P. Šimon, S. Sekretár, *Fett/Lipid* 98 (1996) 60–65.
- [37] G.R. List, T.L. Mounts, F. Orthoefer, W.E. Neff, *J. Am. Oil Chem. Soc.* 72 (1995) 379–382.
- [38] B. Fitch-Haumann, *Inform* 5 (1994) 668–678.

- [39] R. Chowdhury, S. Warnakula, S. Kunutsor, F. Crowe, H.A. Ward, L. Johnson, O.H. Franco, A.S. Butterworth, N.G. Forouhi, S.G. Thompson, K.-T. Khaw, D. Mozaffarian, J. Danesh, E. di Angelantonio, *Ann. Intern. Med.* 160 (2014) 398–406.
- [40] S.J. Baum, P.M. Kris-Etherton, W.C. Willett, A.H. Lichtenstein, L.L. Rudel, K.C. Maki, J. Whelan, Ch.E. Ramsden, R.C. Block, *J. Clin. Lipidol.* 6 (2012) 216–234.
- [41] R. Micha, D. Mozaffarian, *Lipids* 45 (2010) 893–905.
- [42] D.J. McNamara, *J. Am. Coll. Nutr.* 29 (2010) 240s–244s.
- [43] H. Bahrman, B. Fell, G. Papadogianakis, DE 3 942 787 B1 (23.12.1989), EP 0 435 071 B1 (12.12.1990), US 632 465 (1990), CA 2 032 371 (1990), JP Hei/2/402 868 (1990), AU 68 368/90 (1990), BR 90 06 501 (1991), TW 79/109 500 (1990), KO 90/20 650 (1990) to Hoechst AG.
- [44] H. Bahrman, B. Fell, G. Papadogianakis, DE 3 942 954 B1 (23.12.1989), EP 0 435 084 B1 (13.12.1990), US 632 464 (1990), CA 2 032 372 (1990), JP Hei/2/402 869 (1990), AU 68 367/90 (1990), BR 90 06 444 (1991), TW 79/109 499 (1990), KO 90/20 528 (1990) to Hoechst AG.
- [45] B. Fell, G. Papadogianakis, W. Konkol, J. Weber, H. Bahrman, *J. Prakt. Chem./Chem.-Ztg.* 335 (1993) 75–82.
- [46] G. Papadogianakis, Beiträge zur Rhodium-katalysierten Hydroformylierung mittel- und höhermolekularer α -olefine im Ein- und Zweiphasen-System (Ph.D. Thesis), Rheinisch-Westfälische Technische Hochschule (RWTH), Aachen, 1990.
- [47] F. Favre, H. Olivier-Bourbigou, D. Commereuc, L. Saussine, *Chem. Commun.* (2001) 1360–1361.
- [48] G. Papadogianakis, A. Bouriazos, A. Tsihla, Ch. Vasiliou, US 8 334 396 B2 (18.12.2012), EP 2 014 752 A1 (23.06.2007), WO 2009/000435 A1 (14.06.2008), US 2010/0234625 A1 (16.09.2010) to Cognis IP Management GmbH and National and Kapodistrian University of Athens.
- [49] W.M.N. Ratnayake, S.L. Hansen, M.P. Kennedy, *J. Am. Oil Chem. Soc.* 83 (2006) 475–488.
- [50] G. Papadogianakis, A. Bouriazos, K. Mouratidis, N. Psaroudakis, EP 1 918 358 B1 (11.10.2006), US 8 263 794 B2 (11.09.2012), ES 2 391 466 T3 (27.11.2012), WO 2008/043454 A1 (02.10.2007), CA 2 672 680 A1 (17.04.2008) and US 2010/0022664 A1 (28.01.2010) to Cognis IP Management GmbH and National & Kapodistrian University of Athens.
- [51] A. Bouriazos, K. Mouratidis, N. Psaroudakis, G. Papadogianakis, *Catal. Lett.* 121 (2008) 158–164.
- [52] A. Bouriazos, S. Sotiriou, C. Vangelis, G. Papadogianakis, *J. Organomet. Chem.* 695 (2010) 327–337.
- [53] A. Bouriazos, E. Ikonomakou, G. Papadogianakis, *Ind. Crops Prod.* 52 (2014) 205–210.
- [54] N. Nikolaou, Ch.E. Papadopoulos, A. Lazaridou, A. Koutsoumba, A. Bouriazos, G. Papadogianakis, *Catal. Commun.* 10 (2009) 451–455.
- [55] B.R. Moser, M.J. Haas, J.K. Winkler, M.A. Jackson, S.Z. Erhan, G.R. List, *Eur. J. Lipid Sci. Technol.* 109 (2007) 17–24.
- [56] B.R. Moser, A. Williams, M.J. Haas, R.L. McCormick, *Fuel Process. Technol.* 90 (2009) 1122–1128.
- [57] O. Falk, R. Meyer-Pittroff, *Eur. J. Lipid Sci. Technol.* 106 (2004) 837–843.
- [58] R.A. Ferrari, V. da Silva Oliveira, A. Scabio, *Sci. Agric.* 62 (2005) 291–295.
- [59] F. Zaccheria, R. Psaro, N. Ravasio, *Green Chem.* 11 (2009) 462–465.
- [60] P. Pecchia, I. Galasso, S. Mapelli, P. Bondioli, F. Zaccheria, N. Ravasio, *Ind. Crops Prod.* 51 (2013) 306–309.
- [61] K. Wadumesthrige, S.O. Salley, K.Y. Simon, *Fuel Process. Technol.* 90 (2009) 1292–1299.
- [62] N. Numwong, A. Luengnaruemitchai, N. Chollacoop, Y. Yoshimura, *J. Am. Oil Chem. Soc.* 90 (2013) 1431–1438.
- [63] H. Bahrman, B. Cornils, Membrane techniques, in: B. Cornils, W.A. Herrmann (Eds.), *Aqueous-Phase Organometallic Catalysis: Concepts and Applications*, 2nd ed., Wiley-VCH, Weinheim, 2004, pp. 252–255.
- [64] A. Bouriazos, S. Sotiriou, P. Stathis, G. Papadogianakis, *Appl. Catal. B: Environ.* 150–151 (2014) 345–353.